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(54) Title
SECONDARY POLYETHERAMINES, THEIR PRODUCTION AND USE FOR THE PRODUCTION OF POLYUREAS

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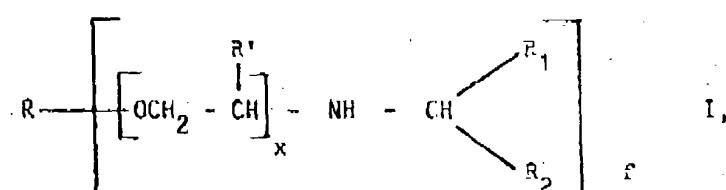
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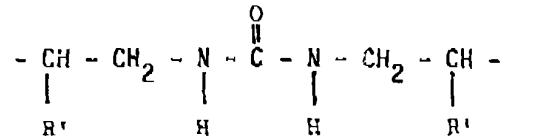
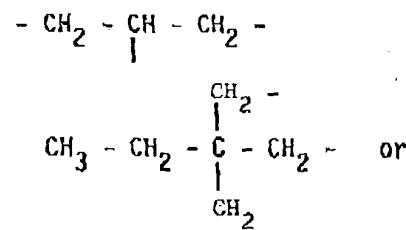
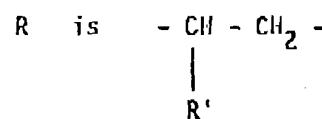
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SPRUS

1. Secondary polyether amines of the general formula



where



R₁ is hydrogen, straight-chain, branched, or cyclic alkyl with 1 to 6 carbon atoms,

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R_2 is branched alkyl with 3 to 10 carbon atoms, furyl-(2), or tetrahydrofuryl-(2),

R_1 and

R_2 together are cyclic alkyl with 5 to 8 carbon atoms, optionally substituted once, twice, or three times with alkyl with 1 to 3 carbon atoms

R' is hydrogen or methyl,

x is 1 - 100 and

f is 2 or 3

2. Process for the production of secondary polyetheramines according to claim 1,

characterized by reacting carbonyl compounds of the general formula



where

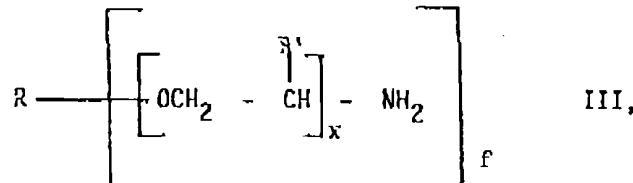
R_1 is hydrogen, straight-chain, branched, or cyclic alkyl with 1 to 6 carbon atoms,

R_2 is branched alkyl with 3 to 10 carbon atoms, furyl-(2), or tetrahydrofuryl-(2),

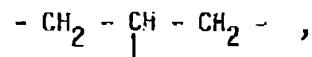
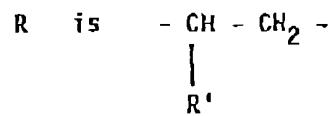
R_1 and

R_2 together are cyclic alkyl with 5 to 8 carbon atoms, optionally substituted once, twice, or three times with alkyl with 1 to 3 carbon atoms

with polyoxyalkylenedi- and triamines of the general formula

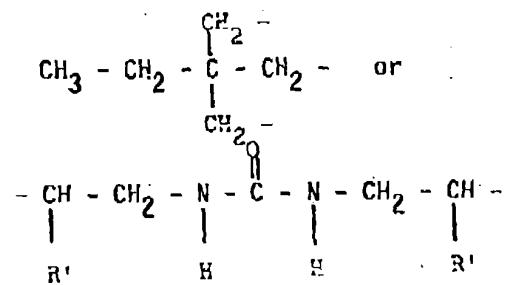


where



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R' is hydrogen or methyl,

x is 1 - 100 and

f is 2 or 3.

With 1 to 30 moles of the carbonyl compound per mole equivalent of the amino compound at a temperature of 55 to 160°C until formation of H₂O is terminated and by hydrogenating under pressure the reaction product in the presence of noble metal catalysts.

FORM 1

619326

SPRUSON & FERGUSON

COMMONWEALTH OF AUSTRALIA
PATENTS ACT 1952
APPLICATION FOR A STANDARD PATENT

RWE-DEA Aktiengesellschaft fur Mineraloel und Chemie, of Uberseering 40,
D-2000 Hamburg 60, FEDERAL REPUBLIC OF GERMANY, hereby apply for the grant of
a standard patent for an invention entitled:

Secondary Polyetheramines, their Production and Use for the
Production of Polyureas

which is described in the accompanying complete specification.

Details of basic application(s):-

Basic Appli. No: Country: Application Date:
P38 25 637.1 DE 28 July 1988

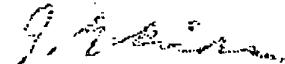
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Sydney New South Wales Australia

DATED this TWENTY SEVENTH day of JULY 1989

RWE-DEA Aktiengesellschaft fur Mineraloel und Chemie

By:



Registered Patent Attorney

TO: THE COMMISSIONER OF PATENTS
OUR REF: 101786
S&F CODE: 58649

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SPRUSON & FERGUSON

COMMONWEALTH OF AUSTRALIA

THE PATENTS ACT 1990

DECLARATION IN SUPPORT OF A
CONVENTION APPLICATION FOR A PATENTIn support of the Convention Application made for a
patent for an invention entitled:Title of Invention Secondary Polyetheramines, their Production and Use
for the Production of PolyureasFull name(s) and
address(es) of
Declarant(s) I/We Dieter Bornemann, Kettwuder Str. 20B, D-2061 Bergfeld-Stegen and
Dr. Wolfgang Reith, S...Nikolaus-Str. 23, D-4170 Geldern-Woldeck
both of Federal Republic of GermanyAUSTRALIA
CONVENTION
STANDARD
& PETTY PATENT
DECLARATION

do solemnly and sincerely declare as follows:-

Full name(s) of
Applicant(s)

1. I am/We are the applicant(s) for the patent

(or, in the case of an application by a body corporate)

1. I am/We are authorised by RWE-DEA Aktiengesellschaft für
Mineralöl und Chemie
the applicant(s) for the patent to make this declaration on
its/their behalf.
2. The basic application(s) as defined by Section 141 of the
Act was/were made

Basic Country(s)

in Federal Republic of Germany

Priority Date(s)

on 28 July 1988

Basic Applicant(s)

by Deutsche Texaco Aktiengesellschaft

Full name(s) and
address(es) of
Inventor(s)3. I am/We are the actual inventor(s) of the invention referred
to in the basic application(s)

(or where a person other than the inventor is the applicant)

3. Heiko Humbert and Detlef Hoell

of Hugo-Klemm-Strabe 23, 2100 Hamburg 90 Federal Republic
of Germany and Homberger Strabe 18, 4130 Moers 1,
Federal Republic of Germany

(respectively)

is/are the actual inventor(s) of the invention and the facts upon
which the applicant(s) is/are entitled to make the application are
as follows:The said applicant is the assignee of the actual
inventors and made the basic application in its
former name of Deutsche Texaco Aktiengesellschaft,
the name of the Company now having been changed.

4. The basic application(s) referred to in paragraph 2 of this
Declaration was/were the first application(s) made in a Convention
country in respect of the invention(s) the subject of the application.

Declared at Moers this 28. day of June 1989
(former Deutsche Texaco Aktiengesellschaft)

RWE-DEA Aktiengesellschaft für Mineralöl und Chemie

SFP4

To: The Commissioner of Patents

Signature of Declarant(s)
Dieter Bornemann Dr. Wolfgang Reith/81

S & F Ref: 101766

FORM 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

COMPLETE SPECIFICATION

619326

(ORIGINAL)

FOR OFFICE USE:

Class Int Class

Complete Specification Lodged:

Accepted:

Published:

Priority:

Related Art:

Name and Address
of Applicant:RWE-DEA Aktiengesellschaft fur Mineraloel und Chemie
Uberseeering 40
D-2000 Hamburg 60
FEDERAL REPUBLIC OF GERMANY

Address for Service:

Spruson & Ferguson, Patent Attorneys
Level 33 St Martins Tower, 31 Market Street
Sydney, New South Wales, 2000, Australia

Complete Specification for the invention entitled:

Secondary Polyetheramines, their Production and Use for the
Production of PolyureasThe following statement is a full description of this invention, including the
best method of performing it known to me/us

5845/3

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Abstract

SECONDARY POLYETHERAMINES, THEIR PRODUCTION AND USE FOR THE PRODUCTION OF POLYUREAS

The invention describes new secondary polyetherpolyamines as well as their production and use. In particular, secondary polyoxypolylenediamines and -triamines are characterized with respect to their properties, synthesis, and applications. This material class allows to build a completely polyurethane-free polyurea compound. The polyoxypolyethylene structure provides the desired flexibility of the polymer and the hydrophobic properties of the polyoxypolyethylene body prevent absorption of water. Due to their high reactivity, the terminal amine groups furthermore allow short reaction times without need for activators. By selection of the substituent on the amine nitrogen the reaction rate of this compound is considerably variable.

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SECONDARY POLYETHERAMINES,
THEIR PRODUCTION AND USE FOR THE PRODUCTION OF POLYUREAS

High-grade polymers are built by reacting terminally functionalized compounds, in the case of polyurethanes normally by reacting polyols and polyfunctional isocyanates. However, this reaction - alcohol and isocyanate - with its many variants is comparably slow and, thus, causes waiting times during the commercial production of such materials. The reaction rate can be increased to a certain extent by addition of activators (also termed catalysts), but when using activators or catalysts, possible incompatibilities of the individual components of the multicomponent system used in practice have to be taken into consideration, such as discoloration with other materials used e.g. as surface materials. Moreover, the normally volatile activators impart an undesired smell to the finished product.

Widely used starting materials today are polyoxypropylene polyols imparting excellent mechanical properties to the end products. A great disadvantage of this material class, namely the low reaction rate during addition to isocyanates, is caused by the secondary nature of the alcohol function.

By addition of ethyleneoxide to polyoxypropylene polyols the secondary alcohol function can be changed into a primary alcohol function yielding so-called tipped polyols. The primary alcohol groups formed have a significantly higher reactivity, but, unfavorably, an overproportionally great quantity of ethyleneoxide is needed to convert as completely as possible the secondary alcohol groups into primary ones. However, due to the high oxyethylene quantity, the pure polyoxypropylene body loses its characteristic properties and, thus, the advantages of the branched alkyl structure, such as hydrophobicity and low crystallinity.

Hence, polymer builders with the advantages of polyoxypropylene (low water absorption) and polyoxyethylene (high reactivity), but without their disadvantages (low reactivity and distinct hydrophilicity) are desired.

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Some of these requirements are fulfilled by polyesterpolyols. The reactivity of the primary alcohol functions as well as the mechanical properties of the polymeric end products meet the requirements set in practice. Unfortunately, however, the ester groups have a weak chemical resistance as a result of their heavily impaired hydrolysis stability. In the presence of water the reversible ester reaction results in reformation of acid groups and alcohol groups with cleavage of the polymer structure and, thus, in embrittlement of the material.

Primary amines have been used for some time as starters and chain extenders, see *Kunststoff-Handbuch* (Plastics Handbook), C. Hanser publishers, Munich/Vienna, 2nd edition, 1983, volume 7 'Polyurethanes', page 18.

Since recently primary aliphatic polyetheramines have been replacing, wholly or in part, the corresponding polyols for producing polyurethanes or polyureas.

In U.S.-PS 4 396 729 terminal amines of polyetherpolyols for the production of reaction injection molded (RIM) elastomers have been disclosed. According to said patent specification, solely primary amines are used and the molded elastomer pieces are produced on the accuration (RIM) machine. For, when exchanging the alcohol function for aliphatic primary amine groups, the reactivity of the reaction with isocyanates increases considerably. Therefore, those amines are only suitable for the RIM process using machines with a special injection technique.

For this reason and others, slower polyurea systems are desired, e.g. for improving the flow of the material injected into the mold at shot times of 0.8 to 1.2 seconds (R.P. Taylor, F. Sanns, Polyurethanes World Congress 1987, Proceedings of the FSK/SPI, p. 219).

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Furthermore, slower systems may be used in existing production facilities with shorter and, thus, improved cycle times than those required for polyurethane RIM systems (R.J.G. Dominguez, D.M. Rice, R.A. Grigsby, Jr., Polyurethanes World Congress 1987, Proceedings of the FSK/SPI, p. 216).

Besides the technological task to control these fast reactions technically, primary amine functions have another disadvantage. Due to the two substitutable hydrogen atoms, primary amines may react like a difunctional group. The aliphatic urea derivatives formed first may undergo crosslinking to form the biuret.

In addition to covalent crosslinking, e.g. by biuret formation, the tertiary structure (morphology) of the polyureas or polyurethanes is also influenced by the sequence of the polymer formation reactions (Kunststoff-Handbuch, vol. 7 'Polyurethanes', chapter 2.5.2: Segmented Polyurethanes, p. 32 ff). This reaction sequence is determined by the different reactivities of the compounds used with respect to isocyanate group.

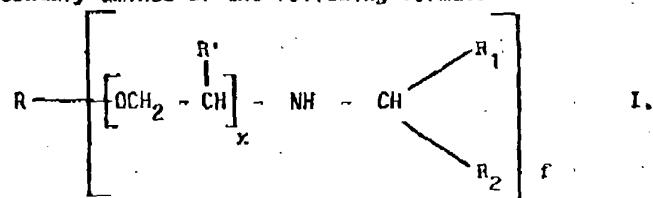
As structural analyses of polyurethanes show, great importance is attached to the formation of hard and soft segments in the polymer to obtain specific properties of the material (J.P. Armistead, G.L. Wilkes, R.B. Turner, Journal of Applied Polymer Science, vol. 35, p. 601-629, 1988).

For instance, it has been demonstrated on a polyurea-RIM-material that there is a change in the relationship between the flexural modulus and the hard segment portion: from a certain hard segment portion the nonlinear relationship between these two quantities changes to a linear one (R.A. Grigsby, D.M. Rice, Proceedings of the SPI, 30th Annual Technical/Marketing Conference, 1986, p. 2). The authors attribute this behavior to the beginning dominating influence of the hard segments on the polymer morphology.

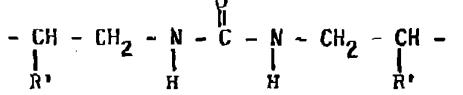
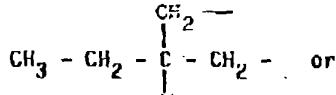
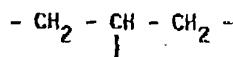
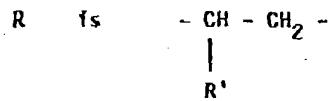
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It is the object of this invention to make available suitable poly-etheramines for producing polyureas, which allow catalyst-free reaction with customary isocyanates as well as production of polyureas with formation and processing rates allowing conversion in conventional processing facilities and controlled variation of the polymer morphology.

According to the invention, this problem is solved by making available secondary amines of the following formula



where



R'_1 is hydrogen, straight-chain, branched, or cyclic alkyl with 1 to 6 carbon atoms, particularly straight-chain or branched alkyl with 1 to 4 carbon atoms, particularly preferred methyl or 2-methyl-1-propyl,

R'_2 is branched alkyl with 3 to 10 carbon atoms, furyl-(2), or tetrahydrofuryl-(2), particularly branched alkyl with 3 to 7 carbon atoms, particularly preferred 2-methyl-1-propyl, 2-propyl or 2,4-dimethyl-1-pentyl,

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 R_1 and R_2 together are cyclic alkyl with 5 to 8 carbon atoms, optionally substituted once, twice, or three times with alkyl with 1 to 3 carbon atoms, R_1 is hydrogen or methyl, x is 1 - 100 and f is 2 or 3

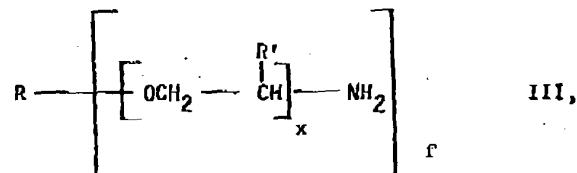
Furthermore, it is the object of this invention to produce said compounds by reacting carbonyl compounds of the general formula



where

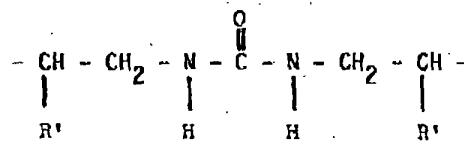
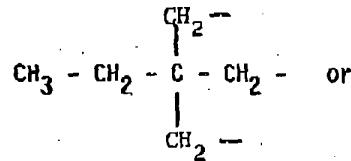
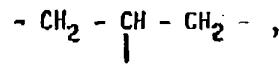
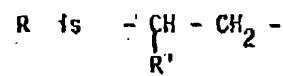
 R_1 is hydrogen, straight-chain, branched, or cyclic alkyl with 1 to 6 carbon atoms, particularly straight-chain or branched alkyl with 1 to 4 carbon atoms, particularly preferred methyl or 2-methyl or 2-methyl-1-propyl, R_2 is branched alkyl with 3 to 10 carbon atoms, or furyl-(2), or tetrahydrofuryl-(2), particularly branched alkyl with 3 to 7 carbon atoms, particularly preferred 2-methyl-1-propyl, 2-propyl or 2,4-dimethyl-1-pentyl, R_1 and R_2 together are cyclic alkyl with 5 to 8 carbon atoms, optionally substituted once, twice, or three times with alkyl with 1 to 3 carbon atoms

with polyoxyalkylenedi- and triamines of the general formula



- 6 -

where

 R' is hydrogen or methyl. x is 1 ~ 100 and f is 2 or 3.

with 1 to 30 moles of the carbonyl compound per mole equivalent of the amino compound at a temperature of 55 to 160 °C until formation of H_2O is terminated and by hydrogenating under pressure the reaction product in the presence of noble metal catalysts.

The invention also refers to the use of these compounds for the catalyst-free reaction with isocyanates for the manufacture of polyurea polymerizates.

The secondary polyetheramines produced according to the invention have a defined functionality and a lower, but still high reactivity, as compared to primary or secondary alcohols. The maintained polyoxypropylene structure ensures that the end product is still highly elastic and unsensitive to hydrolysis.

The phase formation (hard and soft segments) during formation of the polymer structure mainly depends on the reaction rates of the individual components with the isocyanate. Reaction-kinetic

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examinations show that the aliphatic secondary polyetheramines claimed according to the invention surprisingly have about the same reactivity as aromatic diamines, contrary to the analogous primary polyetheramines having a reaction rate that is nearly by two powers of ten faster. Since this material class (e.g. diethyltoluenediamine, DETDA) is often used as a so-called chain extender in the RIM process where it substantially controls the hard segment formation, it is unexpectedly possible to change in a controlled way the morphology of materials composed in this way and, optionally, to influence the dominance of soft or hard segments. When using secondary polyetheramines, the morphology is drastically different in comparison with polymers of primary amine monomers, as a result of the almost parallel reaction of soft and hard segment formers.

The produced secondary polyetherpolyamines optimally meet today's requirements made on materials for building polymers. They stand out from classical polyurethane components by the following properties:

- high selectivity and reactivity
- defined functionality
- chemical and mechanical resistance
- improved thermal stability

In addition to the described improvements, these advantages allow to use new formulations tailored to so-called modern systems and their requirements.

Those systems react without activator, have improved temperature resistance, allow short cycle times, and absorb little water.

With the secondary polyetheramines according to the invention, the reaction rate can be influenced, as desired, in a controlled way by simply choosing the substituent on the amine-nitrogen atom. The kinetic measurements on differently substituted polyoxypropylenediamines described further down show that a certain reactivity of these amines can be arranged without problems. The rate of reaction with isocyanates can be slowed down between 20 and 80 times. By

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mixing the different components the reactivity can be continuously adjusted.

The examples illustrate the applications of the polyurethane-free polyurea systems produced from the secondary polyetheramines according to the invention. Due to the structural variability of the secondary polyoxypropylenopolyamines according to the invention, conventional processing methods can be easily adjusted to the modern requirements of polyurethane technology. Therefore, they are also suitable for all applications of classical polyurethane chemistry, such as rigid foam, soft foam, cold foam, integral foam, microcellular foam, one-component foam, casting elastomers, RIM applications, dispersions, coatings, spray coatings, and adhesives.

Carbonyl compounds with the following properties are particularly suitable for producing the secondary polyetheramines according to the invention:

- boiling point at normal pressure between 60 and 160 °C.
- low miscibility with water,
- formation of a minimum azeotrope with water,
- a branch in alpha or beta position to the carbonyl group, such as

1. 2-methylpropanal
2. 2-methylbutanal
3. 3-methylbutanal
4. 2,2-dimethylpropanal
5. 2-ethylhexanal
6. 3-methyl-2-butanone
7. 4-methyl-2-pentanone
8. 2,2-dimethyl-3-butanone
9. 2,4-dimethyl-3-pentanone
10. 4,6-dimethyl-2-heptanone
11. 2,6-dimethyl-4-heptanone
12. methylcyclopropylketone
13. methylcyclopentylketone
14. methylcyclohexylketone

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15. 2-methylcyclopentanone
16. 2-methylcyclohexanone
17. 2,5-dimethylcyclopentanone
18. 2,6-dimethylcyclohexanone
19. cyclohexanone
20. cyclopentanone

thereof particularly the carbonyl compounds 6, 7, 10, and 11, or a mixture of 10 and 11 (= technical-grade diisobutylketone).

The carbonyl compounds of the general formula II are reacted with primary polyoxyethylene/polyoxypropylene-diamines and -triamines of the general formula III.

These polyoxyalkylenediamines and -triamines have an average molecular weight of about 140 to 5000, preferably about 2000 to 5000, and a functionality (f) of 2 or 3. The group R represents the basic structure of the compounds used for oxyalkylation, such as ethylene glycol, propylene glycol, glycerol, trimethylolpropane, or urea.

The remainder R' is hydrogen in polyoxyethylene compounds or methyl in polyoxypropylene compounds; the index x may be a value of 1 to 100.

Commercially available compounds of this type are the polyoxyalkylenediamines and -triamines marketed by Texaco Chemical Company under the trade name of Jeffamine, such as

| | |
|---------------------------------|---|
| Jeffamine ^(R) D 4000 | (polyoxypropylenediamine; average molecular mass 4000) |
| Jeffamine ^(R) D 2000 | (polyoxypropylenediamine; average molecular mass 2000) |
| Jeffamine ^(R) T 5000 | (polyoxypropylenetriamine; average molecular mass 5000) |
| Jeffamine ^(R) D 400 | (polyoxypropylenediamine; average molecular mass 400) |
| Jeffamine ^(R) D 230 | (polyoxypropylenediamine; average molecular mass 230) |

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Jeffamine^(R) DU 700 (urea-started polyoxypropylenediamine; average molecular mass 700)
Jeffamine^(R) T 403 (polyoxypropylenetriamine; average molecular mass 440).
Jeffamine^(R) EDR 148 (polyoxyethylenediamine; molecular mass 148)
Jeffamine^(R) EDR 192 (polyoxyethylenediamine; molecular mass 192)

The secondary polyetheramines according to the invention are synthesized in a controlled way by a two-stage process. In the first stage, as known per se to the chemist, ketones or aldehydes are reacted with the primary polyetheramines to form the Schiff's bases (azomethines). The ketones or aldehydes used or the external agents added serve as entraining agents for the azeotropic removal of the water formed. The entraining agents form two-phase azeotropes with water which decompose, when eliminated from the system, and are recycled to the process, after removal of the reaction water. The quantity of reaction water allows to check easily when the reaction is complete. The boiling temperature of the entraining agents or carbonyl compounds used ranges between 40 and 160 °C. By addition of suitable entraining agents the desired reaction or boiling temperature can be chosen. For economic reasons those ketones or aldehydes are used which are commercially available and which have the physical properties mentioned above, such as 4-methyl-2-pentanone (MIBK), 3-methyl-2-butanone (MIK), the commercially prepared mixture of 4,6-dimethyl-2-heptanone and 2,6-dimethyl-4-heptanone (DIBK), cyclohexanone, furfural, and 2-methyl-propanal (iso-butyraldehyde).

One to 30 moles of the carbonyl compound per mole equivalent of the amino group are reacted for 2 to 40 hours at temperatures of 55 to 160 °C, at least at the boiling temperature of the carbonyl compounds used and not higher than the decomposition temperature of the process components, until no water is formed any more.

The Schiff's bases formed are hydrogenated, as known to the expert, in continuous or discontinuous operation using noble metal cata-

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lysts, such as Pd, Pt, or Re. Palladium catalysts are particularly suitable, because hydrogenolytic cleavage of the ether bonds is hindered and, thus, hydrogenation of the CN-double bond proceeds with high selectivity. The carrier material may be a mineral substance, e.g. alumina, or carbon in granulated, pelleted, or pulverized form. The catalyst concentration, referring to the material to be hydrogenated, is 0.1 to 5 wt.%.

For discontinuous operation particularly an agitated autoclave is used which is filled with about 0.5 wt.% catalyst, referring to the material to be hydrogenated, and with the Schiff's base as a substance or in a solvent, preferably in the ketone/aldehyde and/or the corresponding secondary alcohol of the hydrogenated starting component, used for the reaction. Hydrogenation takes place at a pressure of 60 to 180 bar, preferably 100 to 140 bar, and a temperature of 100 to 200 °C, preferably 140 to 160 °C.

Also for continuous hydrogenation, e.g. in a downstream reactor, noble metal catalysts of the above mentioned type are used. A typical catalyst contains 5 wt.% Pd, referring to alumina. Suitable reaction conditions are temperatures of 100 to 220 °C, preferably 150 to 175 °C, a pressure of 60 to 120 bar, preferably 100 bar, and a liquid hourly space velocity (LHSV) of 1 liter of liquid volume/hour and liter of reactor volume.

The following examples illustrate production and use of the compounds according to the invention. The molecular masses stated therein are statistical mean values.

Example 1

N,N'-bis(4-methyl-2-pentyl)-polyoxypropylenediamine;
molecular mass 390.

Quantity weighed in: 87.6 kgs of polyoxypropylenediamine with a
molecular mass of 230 (Jeffamine^(R) D 230),
152.5 kgs of 4-methyl-2-pentanone

Total quantity: 240.1 kgs

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The starting materials were filled together into an agitated reactor and were heated to the boiling point. Dehydration started at a temperature in the reactor sump of about 115 °C. The distilling 4-methyl-2-pentanone was recycled to the reactor. The end of reaction was recognizable by the amount of water formed (about 10.5 liters); the reaction time was 29 hours.

The excess 4-methyl-2-pentanone then was distilled off at normal pressure. During this operation the sump temperature increased from 139 °C to 161 °C. After 6 hours 165 kgs of the azomethine remained and were directly led to hydrogenation.

In a continuously operated hydrogenation apparatus with a capacity of 4 liters and a catalyst zone of 9 meters, packed with 5 % Pd on Al_2O_3 , the intermediate product was hydrogenated within 50 h at a temperature of 151-153 °C and a pressure of 100 bar. The crude product thus obtained was freed from volatile components at 112 °C and 24 mbar during 10 hours while passing through N_2 .

141 kgs of N,N' -bis(4-methyl-2-pentyl)-polyoxypropylenediamine (molecular mass 390) remained.

Physical data: Total amines: 5.1 meq/g
 Refractive index: n_{D}^{20} 1.4436
 Water content: 0.2 %
 Viscosity: 13 mPa.s

Example 2

N,N' -bis(4-methyl-2-pentyl)-polyoxypropylenediamine;
molecular mass 560

Quantity weighed in: 42.6 kgs of polyoxypropylenediamine with a molecular mass of 400 (Jeffamine^(R) D 400),
53.4 kgs of 4-methyl-2-pentanone

Total quantity: 96.0 kgs

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The starting materials were filled together into the reactor and were heated to the boiling point. Dehydration started at a temperature in the reactor sump of about 110 °C. The distilling 4-methyl-2-pentanone was recycled to the reactor. The end of reaction was recognizable by the amount of water formed (about 3.4 liters); the reaction time was 22 hours.

The excess 4-methyl-2-pentanone then was distilled off at normal pressure. During this operation the sump temperature increased from 146 °C to 163 °C. After 3 hours 65 kgs of the azomethine remained and were directly led to hydrogenation.

In a continuously operated hydrogenation apparatus as described in example 1 the intermediate product was hydrogenated within 100 h at a temperature of 150 °C and a pressure of 100 bar. The crude product thus obtained was freed from volatile components at 160 °C and 25 mbar during 7 hours while passing through N₂. 56 kgs of N,N'-bis(4-methyl-2-pentyl)-polyoxypropylenediamine (molecular mass 560) remained.

| | | |
|----------------|-------------------|---------------------|
| Physical data: | Total amines: | 3.2 meq/g |
| | Refractive index: | n_{D}^{20} 1.4464 |
| | Water content: | 0.1 % |
| | Viscosity: | 33 mPa.s |

Example 3

N,N'-bis(4-methyl-2-pentyl)-polyoxypropylenediamine;
molecular mass 2150

Quantity weighed in: 138.6 kgs of polyoxypropylenediamine with a
molecular mass of 2000 (Jeffamine^(R) D 2000),
101.4 kgs of 4-methyl-2-pentanone

Total quantity: 240.0 kgs

The starting materials were filled together into the reactor and were heated to the boiling point. Dehydration started at a tempera-

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ture in the reactor sump of about 96 °C. The distilling 4-methyl-2-pentanone was recycled to the reactor. The end of reaction was recognizable by the amount of water formed (about 2 liters); the reaction time was 16 hours.

The excess 4-methyl-2-pentanone then was distilled off at normal pressure. During this operation the sump temperature increased from 127 °C to 160 °C. After 5 hours 164 kgs of the azomethine remained in the reactor. The intermediate product was directly led to hydrogenation.

In a continuously operated hydrogenation apparatus as described in example 1 the intermediate product was hydrogenated within 47 hours at a temperature of 167-168 °C and a pressure of 100 bar. The crude product thus obtained was freed from volatile components at 112 °C and 23 mbar during 6 hours while passing through N₂. 140 kgs of N,N'-bis(4-methyl-2-pentyl)-polyoxypropylenediamine (molecular mass 2150) remained.

Physical data: Total amines: 0.93 meq/g
 Refractive index: n_{D20} 1.4497
 Water content: 0.05 %
 Viscosity: 350 mPa.s

Example 4

N,N',N"-tris(4-methyl-2-pentyl)-polyoxypropylenetriamine;
molecular mass 700

Quantity weighed in: 93.16 kgs of trimethylolpropane-polyoxypropylene adduct triamine with a molecular mass of 440 (Jeffamine^(R) T 403),
146.84 kgs of 4-methyl-2-pentanone

Total quantity: 240.0 kgs

The starting materials were filled together into the reactor and were heated to the boiling point. Dehydration started at a tempera-

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ture in the reactor sump of about 115 °C. The distilling 4-methyl-2-pentanone was recycled to the reactor. The end of reaction was recognizable by the amount of water formed (about 9 liters); the reaction time was 26 hours.

The excess 4-methyl-2-pentanone then was distilled off at normal pressure. During this operation the sump temperature increased from 127 °C to 160 °C. After 8 hours 154 kgs of the azomethine remained in the reactor. The intermediate product was directly led to hydrogenation.

In a continuously operated hydrogenation apparatus as described in example 1 the intermediate product was hydrogenated within 48 hours at a temperature of 169-171 °C and a pressure of 100 bar. The crude product thus obtained was freed from volatile components at 108 °C and 25 mbar during 7 hours while passing through N₂. 137 kgs of N,N',N"-tris(4-methyl-2-pentyl)-polyoxypropylenetriamine (molecular mass 700) remained.

Physical data: Total amines: 4.3 meq/g
Refractive index: n_{D}^{20} 1.4526
Water content: 0.02 %
Viscosity: 84 mPa.s

Example 5

N,N',N"-tris(4-methyl-2-pentyl)-polyoxypropylenetriamine;
molecular mass 5250

Quantity weighed in: 143.0 kgs of trimethylolpropane-polyoxypropylene adduct triamine with a molecular mass of 5000 (Jeffamine^(R) T 5000),
97.0 kgs of 4-methyl-2-pentanone

Total quantity: 240.0 kgs

The starting materials were filled together into the reactor and were heated to the boiling point. Dehydration started at a tempera-

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ture in the reactor sump of about 119 °C. The distilling 4-methyl-2-pentanone was recycled to the reactor. The end of reaction was recognizable by the amount of water formed (about 1.2 liters); the reaction time was 6 hours.

The excess 4-methyl-2-pentanone then was distilled off at normal pressure. During this operation the sump temperature increased from 124 °C to 160 °C. After 6 hours 161 kgs of the azomethine remained. After addition of 15 liters of 4-methyl-2-pentanol, the intermediate product was led to hydrogenation.

In a continuously operated hydrogenation apparatus as described in example 1 the intermediate product was hydrogenated within 197 h at a temperature of 169-170 °C and a pressure of 100 bar. The crude product thus obtained was freed from volatile components at 110 °C and 25 mbar during 4 hours while passing through N₂. 136 kgs of N,N',N"-tris(4-methyl-2-pentyl)-polyoxypropylenetriamine (molecular mass 5250) remained.

Physical data: Total amines: 0.5 meq/g
 Refractive index: n_{D}^{20} 1.4519
 Water content: 0.03 %
 Viscosity: 1150 mPa.s

The following secondary polyetheramines were produced accordingly, the difference being that the hydrogenation was performed in batches.

Example 6

N,N'-bis(cyclohexyl)-polyoxypropylenediamine, molecular mass 560, produced by reaction of Jeffamine^(R)_D 400 with cyclohexanone

Total amines: 3.15 meq/g
Refractive index: n_{D}^{20} 1.4660
Water content: 0.04 %
Viscosity: 89 mPa.s

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Example 7

N,N' -bis(cyclohexyl)-polyoxypropylenediamine, molecular mass 2150, produced by reaction of Jeffamine^(R)_D 2000 with cyclohexanone

Total amines: 0.90 meq/g
Refractive index: n_{D}^{20} 1.4556
Water content: 0.01 %
Viscosity: 450 mPa.s

Example 8

N,N' -bis(isononyl)-polyoxypropylenediamine, molecular mass 2250, produced by reaction of Jeffamine^(R)_D 2000 with technical-grade diisobutyl ketone

Total amines: 0.90 meq/g
Refractive index: n_{D}^{20} 1.4509
Water content: 0.01 %
Viscosity: 392 mPa.s

Example 9

N,N' -bis(3-methyl-2-butyl)-polyoxypropylenediamine, molecular mass 2120, produced by reaction of Jeffamine^(R)_D 2000 with 3-methyl-2-butanone

Total amines: 0.85 meq/g
Refractive index: n_{D}^{20} 1.4505
Water content: 0.1 %
Viscosity: 336 mPa.s

Example 10

N,N' -bis(2-methyl-1-propyl)-polyoxypropylenediamine, molecular mass 2100, produced by reaction of Jeffamine^(R)_D 2000 with iso-butyraldehyde

Total amines: 0.86 meq/g
Refractive index: n_{D}^{20} 1.4511
Water content: 0.08 %
Viscosity: 391 mPa.s

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Example 11

N,N'-bis(4-methyl-2-pentyl)-polyoxypropylenediamine, molecular mass 390, produced by reaction of Jeffamine^(R)D 230 with 4-methyl-2-pentanone

Total amines: 5.0 meq/g
Refractive index: n_{D}^{20} 1.4443
Water content: 0.13 %
Viscosity: 12 mPa.s

Example 12

N,N'-bis(4-methyl-2-pentyl)-polyoxypropylenediamine, molecular mass 560, produced by reaction of Jeffamine^(R)D 400 with 4-methyl-2-pentanone

Total amines: 3.26 meq/g
Refractive index: n_{D}^{20} 1.4463
Water content: 0.08 %
Viscosity: 32 mPa.s

Example 13

N,N'-bis(4-methyl-2-pentyl)-polyoxypropylenediamine, molecular mass 2150, produced by reaction of Jeffamine^(R)D 2000 with 4-methyl-2-pentanone

Total amines: 0.86 meq/g
Refractive index: n_{D}^{20} 1.4505
Water content: 0.14 %
Viscosity: 300 mPa.s

Example 14

N,N'-bis(4-methyl-2-pentyl)-polyoxypropylenediamine, molecular mass 4140, produced by reaction of Jeffamine^(R)D 4000 with 4-methyl-2-pentanone

Total amines: 0.43 meq/g
Refractive index: n_{D}^{20} 1.4508
Water content: 0.01 %
Viscosity: 1173 mPa.s

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Example 15

N,N',N'' -tris(4-methyl-2-pentyl)-polyoxypropylenetriamine, molecular mass 700, produced by reaction of Jeffamine^(R)_T 403 with 4-methyl-2-pentanone

Total amines: 4.3 meq/g
Refractive index: n_{D}^{20} 1.4532
Water content: 0.1 %
Viscosity: 88 mPa.s

Example 16

N,N',N'' -tris(4-methyl-2-pentyl)-polyoxypropylenetriamine, molecular mass 5250, produced by reaction of Jeffamine^(R)_T 5000 with 4-methyl-2-pentanone

Total amines: 0.45 meq/g
Refractive index: n_{D}^{20} 1.4518
Water content: 0.15 %
Viscosity: 1106 mPa.s

Example 17

Kinetic measurements

Comparison of N,N' -bis(4-methyl-2-pentyl)-polyoxypropylenediamine (molecular mass 2150), N,N' -bis(cyclohexyl)-polyoxypropylenediamine (molecular mass 2150), and N,N' -bis(isononyl)-polyoxypropylenediamine (molecular mass 2250) with Jeffamine^(R)_D 2000 in the reaction with phenylisocyanate

The rate of the reaction of isocyanates with alkylated polyetheramines and with the corresponding primary polyetheramines can be determined by IR-spectroscopy. To this end a phenylisocyanate solution in a known concentration was mixed with a standardized solution of the corresponding polyetheramine and the decrease in isocyanate absorption was followed by IR-spectroscopy.

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Since the reaction proceeds very quickly, a satisfactory resolution time had to be arranged by suitable dilution. The solutions had the following concentrations:

Phenylisocyanate solution: 0.006 mole/l
Polyetherdiamine solution: 0.002 mole/l

The sensitivity problem when recording the IR-spectrum which is due to the high dilution was minimized by a suitable solvent (CCl_4). Near the isocyanate absorption at a wave length of $\nu = 2260 \text{ cm}^{-1}$ carbon tetrachloride does not show absorption.

The reaction mixture was prepared by mixing 1.5 parts of phenylisocyanate solution and 1 part of polyetherdiamine solution resulting in the following starting values during the reaction:

phenylisocyanate concentration: 0.0036 mole/l
polyetherdiamine concentration: 0.0008 mole/l

The results were evaluated on the assumption that the amino groups of the polyetherdiamine react like two independent reactive groups in a bimolecular reaction.

The following compounds were examined and compared with each other:

N,N' -bis(4-methyl-2-pentyl)-polyoxypolylenediamine
(molecular mass 2150)
 N,N' -bis(cyclohexyl)-polyoxypolylenediamine (molecular mass 2150)
 N,N' -bis(isononyl)-polyoxypolylenediamine (molecular mass 2250)
Jeffamine^(R)_D 2000 primary polyetherdiamine
(molecular mass 2000)

In the evaluation the rate coefficient was obtained from the gradient of the logarithmically plotted data.

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The following rate coefficients were obtained after regression analysis of the converted measurement results:

N,N' -bis(4-methyl-2-pentyl)-polyoxypropylenediamine
(molecular mass 2150);
 $k = 2.4 \pm 0.3 \text{ liter} \times \text{mole}^{-1} \text{s}^{-1}$

N,N' -bis(cyclohexyl)-polyoxypropylenediamine
(molecular mass 2150)
 $k = 5.8 \pm 1.6 \text{ liter} \times \text{mole}^{-1} \text{s}^{-1}$

N,N' -bis(isononyl)-polyoxypropylenediamine
(molecular mass 2250)
 $k = 1.8 \pm 0.3 \text{ liter} \times \text{mole}^{-1} \text{s}^{-1}$

The isocyanate reaction of the primary polyetherdiamine could not be measured as a result of the short reaction time, but the rate constant of the primary diamine (Jeffamine^(R) D 2000) can be estimated to be k greater than/equal to $30 \text{ liters} \times \text{mole}^{-1} \text{s}^{-1}$.

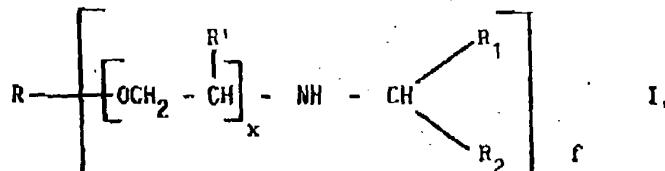
Compared to the unsubstituted compound, the secondary polyetheramines according to the invention have a reaction time extended at least by the factor 5 to 10. Controlled variation of the reaction time is possible by choosing the alkyl substituent.

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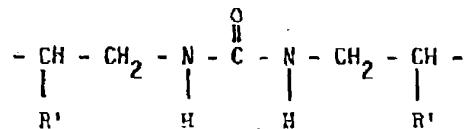
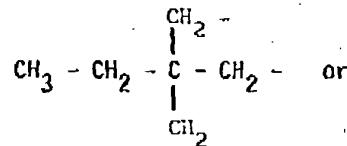
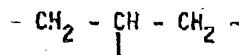
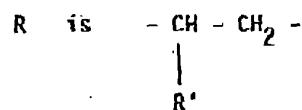
PATENT CLAIMS

The claims defining the invention are as follows:

1. Secondary polyether amines of the general formula



where



R_1 is hydrogen, straight-chain, branched, or cyclic alkyl with 1 to 6 carbon atoms,

R_2 is branched alkyl with 3 to 10 carbon atoms, furyl-(2), or tetrahydrofuryl-(2),

R_1 and

R_2 together are cyclic alkyl with 5 to 8 carbon atoms, optionally substituted once, twice, or three times with alkyl with 1 to 3 carbon atoms

R' is hydrogen or methyl,

x is 1 - 100 and

f is 2 or 3

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2. Process for the production of secondary polyetheramines according to claim 1.

characterized by reacting carbonyl compounds of the general formula



where

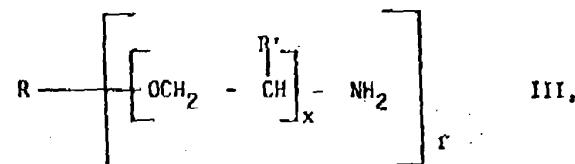
R_1 is hydrogen, straight-chain, branched, or cyclic alkyl with 1 to 6 carbon atoms.

R_2 is branched alkyl with 3 to 10 carbon atoms, furyl-(2), or tetrahydrofuryl-(2),

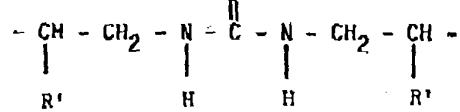
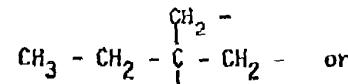
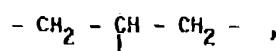
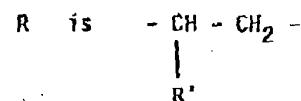
R, and

R_2 together are cyclic alkyl with 5 to 8 carbon atoms, optionally substituted once, twice, or three times with alkyl with 1 to 3 carbon atoms

with polyoxyalkylenedi- and triamines of the general formula



where



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R¹ is hydrogen or methyl,

x is 1 - 100 and

f is 2 or 3,

with 1 to 30 moles of the carbonyl compound per mole equivalent of
5 the amino compound at a temperature of 55 to 160°C until formation
of H₂O is terminated and by hydrogenating under pressure the
reaction product in the presence of noble metal catalysts.

10 3. Secondary polyether amines substantially as hereinbefore
described with reference to any one of the Examples.

15 4. A process for preparing secondary polyether amines
substantially as hereinbefore described with reference to any one of the
Examples.

5. The product of the process of claim 2.

6. A catalyst-free method of manufacturing polyureas, said method
15 comprising reacting secondary polyether amines according to claim 1 or 3
with isocyanates.

DATED this FOURTH day of SEPTEMBER 1991

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TMS/1715R